

KINGDOM OF BELGIUM

707567

No. 707,567

International Classification:

C 07 c

Patent released on:

06-05-1968

MINISTRY OF ECONOMIC AFFAIRS

PATENT

The Minister of Economic Affairs,

Pursuant to the law of May 24, 1854 pertaining to patents;

Pursuant to the Union Convention for the Protection of Industrial Property;

Pursuant to the record drawn up on December 5, 1967, at 3:10 pm

at the Industrial Property Office;

DECREES:

Article 1. - *That the company named: HALCON INTERNATIONAL, INC., 2 Park Avenue, New York, New York 10016 (United States of America), represented by Mr. P. Hanssens in Brussels,*

is hereby granted a patent for: Controlled oxidation of ethylene oxide,

which, according to the Company, is the subject of a patent application filed in the United States of America on December 9, 1966, No. 600,407, under the name of Messrs. D. Brown, J. V. Porcelli, Jr., and Ms. E. R. Flaster, the latter being the claimant.

Article 2.- *This patent is issued to the above-mentioned company without being subject to a preliminary review, at its own risks, and without any guarantee either as to the reality, novelty or merit of the invention, or as to the accuracy of the description, and without prejudice to the rights of third parties.*

A copy of the specification of the invention (description and any drawings) signed by the interested party and filed in support of its application for a patent shall remain attached to this decree.

Brussels, June 5, 1968.

ACTING ON SPECIAL AUTHORITY:

The Director General,

/Signed/

PATENT

Company named:
HALCON INTERNATIONAL, INC.

Controlled oxidation of ethylene oxide
=====

International Convention – Priority of patent application filed in the United States of America on December 9, 1966 under Serial No. 600,407, under the names of David BROWN, Joseph V. PORCELLI, Jr., and Edith Reid FLASTER.

ABSTRACT

This invention pertains to a process for the production of ethylene oxide by the silver catalyzed, controlled oxidation of ethylene with molecular oxygen, where ethane is used as a substantial component of the gas feed to the reaction zone. The invention makes possible the direct catalytic oxidation of ethylene in which ethane is present as an impurity, and thus reduces the financial burden related to the removal of ethane in current state-of-the-art ethylene oxide production processes. The invention also makes it possible to use higher concentrations of oxygen, by obtaining improved selectivity and productivity of ethylene oxide compared to the use of regular diluents such as nitrogen, argon, and methane.

DESCRIPTION

This invention relates to the production of ethylene oxide. More particularly, the invention relates to the silver catalyzed, controlled oxidation of ethylene into ethylene oxide through the use of a reaction gas feed where ethane is a substantial component, i.e. where ethane represents at least 10 mol% of the total gas feed to the reaction zone.

It is well-known that the silver catalyzed oxidation of ethylene to ethylene oxide with molecular oxygen can be controlled by the use of diluents such as nitrogen, carbon dioxide, steam, and other gaseous materials, inert under the conditions of the reaction, in the reaction zone. However, while some degree of control is thereby maintained over the reaction, and

controlled oxidation of ethylene to ethylene oxide may be effected, the conversion of ethylene and the selectivity of the reaction are such that there is room for considerable improvement.

It is taught in the prior art that the presence of methane in the diluent material may make it possible to obtain additional control, with the attendant advantage of improved efficiency. However, even this process suffers from the disadvantage of requiring substantially pure ethylene feedstock since the inclusion of other saturated hydrocarbons normally present, such as ethane, is regarded as particularly harmful to the selectivity of the reaction and as exerting a decidedly depressing effect upon ethylene oxide yield. In fact, the prior art goes far beyond theoretical conjecture and offers seemingly clear and convincing empirical data to support this uncompromising position that optimum production rate is achieved in the total absence of ethane and that, as the ethane content of the total feed to the reactor is increased, the production rate is substantially decreased. It is also taught in the prior art that ethane causes reduced production rates and should be maintained below 1 mol%, and preferably below 0.2 mol% of the total feed to the reaction. Accordingly, even in those ethylene oxide processes where oxidation is effected with high purity oxygen, i.e., at least about 85 mol%, small quantities of ethane in the ethylene feedstock tend to be detrimental in that the overall yield of ethylene oxide produced is thereby substantially reduced. Generally, minimization of ethane in ethylene feed is effected by the installation of auxiliary scrubbing equipment for removal of paraffins from the feed ethylene. The cost of such installation and equipment, and the operation thereof, impose a significant economic burden on the manufacturer.

Other removal treatments may comprise such unit operations as distillation, absorption, adsorption, extraction, etc.. It has also been suggested that molecular sieves, such as the highly porous adsorbents composed of crystalline sodium and calcium aluminosilicates, after heating to remove water of hydration, be employed to preferentially adsorb ethylene, the adsorbed ethylene being thereafter stripped for recycling purposes by means of an inert gas at elevated temperature. Whatever the technique employed, it is apparent that additional equipment and processing operations are required which impair the overall efficiency and economy of the overall ethylene oxide production process.

This is why one of the main purposes of this invention is to provide an improved process for the production of ethylene oxide that does not include the foregoing disadvantages of the prior art.

Another purpose of the invention is to provide a process for the production of ethylene oxide through the direct catalytic oxidation of impure ethylene.

Yet another purpose of the invention is to provide a process for the production of ethylene oxide that employs ethane as a reaction gas heat capacity modifier.

Another purpose of the invention is also to provide a process for the production of ethylene oxide in which a high concentration of oxygen may be employed in the reaction gas mixture to improve productivity.

Other purposes of the invention will also emerge from reading the following detailed description and the claims below.

Generally, the present invention pertains to a process for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, in which ethane is provided as a component of the total feed to the reaction, in an amount of at least 10 mol% of said feed. The ethane employed in the process may be introduced in the ethylene feedstock, in which ethane is present as an impurity, or the ethane may be introduced to the reaction gas from a separate source. Furthermore, the ethane may be introduced to the reaction gas partially as an impurity in the ethylene feedstock and partially as an independent feed stream from a separate source. Regardless of how the ethane is introduced to the process, the process is operated in such manner as to achieve a relatively high concentration of ethane in the gas in the reaction zone. As a result of such operation, higher productivities may be achieved by permitting the use of higher oxygen concentrations. Since oxygen exerts a nominal influence on selectivity and reaction rate, improved productivity is obtainable without an attendant penalty.

Furthermore, as the ethane serves to moderate the peak reaction temperature, the reaction selectivity may also be improved. The use of ethane in the reaction gas together with optimum temperature and/or partial pressure of catalyst activity inhibitor may result in a substantial economic improvement over known processes wherein ethane is removed from the feedstock prior to catalytic oxidation of ethylene.

More specifically, the invention comprises a process for the production of ethylene oxide by vapor phase reaction of ethylene and oxygen, wherein the feed to the reaction comprises ethylene, oxygen, and at least 10 mol% ethane. Obviously, the concentration of oxygen in the reaction gas mixture must be such as to fall short of the flammable limit, i.e. the concentration at which combustion or even explosion may occur. This limit may also be regarded as the point

where zero selectivity or complete oxidation can occur initially. Ethane permits broader ranges than the prior use of nitrogen, argon, or methane.

In carrying out the invention, the components in the total feed to the reaction, expressed as mol or volume percent, may be:

	<u>broad</u>	<u>desirable</u>	<u>preferred</u>
ethylene	4-40	6-35	15-30
oxygen	6-15	8-14	10-13
ethane	10-80	20-70	40-60

In a practical application of the invention, the best results are obtained when a catalyst activity inhibitor, such as ethylene dichloride, is added to the gas mixture. It is generally useful to employ an inhibitor in the reaction gas mixture in an amount of 1 to 100 ppm (parts per million) by weight, more so from 5 to 70 ppm, and preferably from 10 to 20 ppm.

In addition to ethylene dichloride, the preferred inhibitor, other agents capable of exerting an inhibiting effect upon the catalytic oxidation reaction may be utilized. The latter include other halogen-containing compounds, including chlorinated hydrocarbons, as well as chlorinated polyphenyl compounds. However, unlike the prior art teachings, the amounts of such compounds which may suitably be used in the process of the present invention are not limited to relatively small quantities, for example less than 10 ppm, but may include quantities greater than 10 ppm, for example up to 100 ppm. Also, mixtures of the various inhibitors used until now may be usefully employed in the process of the invention.

In one embodiment of the invention, when starting with a commercial ethylene fraction containing a substantial amount, at least 10 mol%, of normally gaseous paraffins having more than one carbon atom, the ethylene in its impure commercial form is fed directly into the reaction zone.

In the production of ethylene oxide by the silver-catalyzed controlled oxidation of ethylene with molecular oxygen in accordance with the invention, the reactants comprising ethylene, oxygen and ethane are passed over a catalyst containing metallic silver at conditions of temperature and pressure resulting in the interaction of ethylene and oxygen with the formation of reaction products comprising ethylene oxide.

The catalysts employed in the process of the invention comprise any of the silver metal-containing catalysts disclosed in the prior art, capable of catalyzing the controlled oxidation, with

molecular oxygen, of ethylene to ethylene oxide. These comprise the catalysts consisting essentially of silver metal upon a suitable support. Suitable supports comprise, for example, any of the siliceous and aluminous support materials employed until now. Particularly suitable catalysts comprise those consisting essentially of silver metal upon such supports as alundum, silicon carbide, silica, carborundum, any of the many alumina supports, etc. Suitable catalysts comprise, for example, those disclosed and claimed in the U.S. Patents 3,207,700 and 2,752,362. It should be understood, however, that the present invention is in no way limited to the use of any specific silver metal-containing catalyst.

The silver metal catalyst used in the process of the invention may be in the form of a stationary bed, or it may be used in fluidized or suspended form. The process is applicable to the use of several catalytic oxidation zones, arranged in series or in parallel. When using several such zones, the reactants and/or added ethane may be introduced into one or more of these zones. Conditions within such zones need not be the same, and may be varied, while reaction products may be separated or not between such zones. Any part or all of the reactants, ethane and/or diluent materials may be introduced into one or more of the reaction zones at more than one point thereof.

The controlled oxidation reaction is carried out at temperatures in the range from approximately 150 to 450°C, for example, and preferably from approximately 200 to 300°C. Pressures ranging from atmospheric to approximately 35 atm. abs. are generally employed, while a range of approximately 17.5 to 24.5 atm. abs. is preferred. Higher pressures may however be used, while remaining within the range of the invention. Diluent materials such as, for example, nitrogen, carbon dioxide, steam, etc., may be present in varying amounts. Such diluents may be introduced into the systems as needed, alone or together with ethane and/or unreacted ethylene taken from the reactor effluent.

The molecular oxygen employed as a reactant in the process may be obtained from any suitable source. The suitable oxygen charge may consist essentially of relatively pure oxygen or a concentrated oxygen stream comprising molecular oxygen in major amount with a lesser amount of one or more diluent inert gases, such as, for example, nitrogen, argon, etc. A preferred concentrated oxygen gas, suitable for use as the make-up oxygen reactant in the process of the invention, comprises the concentrated oxygen gas consisting essentially of oxygen, nitrogen and argon obtained from air, for example, by suitable separating means comprising one or more steps

such as fractionation, low temperature distillation, and other conventional separating means. The suitable gas containing oxygen must preferably have an oxygen concentration of at least 85 mol%. Since the amount of gaseous materials which must be vented from the oxidation process varies directly with the increase in inert gaseous diluents introduced, and since any increase in materials vented is generally accompanied by a decrease in yield of ethylene oxide from the ethylene feed, it is preferred to employ molecular oxygen gas having higher values of oxygen concentration, such as, for example, approximately 85 to 98 mol%. In particular, it is preferred to use a concentrated oxygen gas containing approximately 90 to 97 mol% of molecular oxygen. The concentration of oxygen in the total feed to the ethylene zone may vary, while remaining within the range of the invention. Generally the concentration need not exceed 12 mol% of the total reactor feed. As mentioned previously, care must be exercised to maintain the oxygen concentration in the charge below the flammable limit for the specific conditions employed.

The process of the invention may be applied with a relatively broad concentration of ethylene in the total charge to the reaction zone. Thus, ethylene may constitute, for example, roughly from 4 to 40 mol% of the total feed to the ethylene reaction zone. A concentration of ethylene in the total reactor feed of approximately 6 to 35 mol% is desirable, while 15 to 30 mol% is particularly preferred. However, higher or lower ethylene concentrations may be used, while remaining within the range of the invention. Maintaining a specifically desired ethylene concentration is facilitated by the controlled addition of ethane and by controlling the amount of materials, such as, for example, methane, nitrogen, carbon dioxide, argon, etc., recycled within the system.

Surprisingly, it has been determined that contrary to the prior art, it is unnecessary to maintain a critical mol ratio of ethylene to oxygen in excess of 1 in the total feed to the reaction zone. Furthermore, irrespective of relative ethylene/oxygen concentrations, it is possible to use reactor tubes made of carbon steel, as well as tubes made of alloy steel.

Therefore, the benefits of improved efficiency and productivity inherent in the application of this invention are achieved with controls that are less strict and less complicated than those required by prior art processes.

The key to achieving the objectives of the invention is to include a substantial proportion of ethane, at least 10 mol%, in the total feed to the ethylene reaction zone. The ethane introduced in the system may be obtained from any suitable source. It should be noted that, in contrast to the

methane process of the prior art mentioned above, the presence of paraffinic hydrocarbons other than ethane is not detrimental to the achievement of the purpose of the present invention. Suitable sources of ethane comprise, for example, natural gas, normally gaseous by-product streams containing ethane with or without other paraffins, obtained in thermal hydrocarbon conversion processes, etc. Where ethane is introduced into the system from an independent source, it may be combined directly with part or all of the make-up ethylene, with the recycle stream, or with the feed at the point of entry into the oxidation zone. Part or all of such ethane entering the system may be introduced as a separate stream into the reaction zone along one or more points along the length of said zone.

During the research process that led to this invention, different test production runs were carried out.

The first ethylene oxide production test was conducted for the purpose of providing a standard or reference base where substantially no ethane is contained in the total feed to the ethylene oxidation zone.

In this test, ethylene was oxidized to ethylene oxide by reacting ethylene with molecular oxygen in the presence of a supported silver metal catalyst at a temperature of 250°C and a pressure of 22.05 atm. abs. The make-up ethylene charge consisted essentially of 100% ethylene at a flow rate of 517.56 g per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen fed at a rate of 753.64 g per hour. An independent fresh nitrogen charge, substantially 100% nitrogen, at a flow rate of 4.54 g per hour, completed the make-up charge streams. Recycle gas was added to the make-up gas streams at a flow rate of 23,017.8 g per hour. This recycle gas had a molar composition of 15.2% ethylene, 4.6% oxygen, 7.4% carbon dioxide, 32% argon, and 40.8% nitrogen. The resulting total feed to the reactor flowed at a rate of 24,889 g per hour, and had a molar composition of 17% ethylene, 7.5% oxygen, 7% carbon dioxide, 30% argon, and 38.5% nitrogen. 0.5 ppm by weight of ethylene dichloride was added to this feed. The ethylene oxide was recovered from the reactor effluent by absorption in water, followed by distillation of the rich aqueous absorbate. The residual reactor gaseous effluent, free of reaction products comprising ethylene oxide, was returned as recycle gas to the reaction, with the exception of a small constant bleed from the system. The determination of the difference between the outlet and inlet ethylene oxide at the reactor provided a Δ EO value of 1.75. The Δ

EO value is commonly used as a benchmark, since it is proportional to the ethylene oxide productivity. The overall yield of this example was 68.6%.

A first test according to the invention was conducted with ethane present in the total feed, in substantial amount as a ballast. In this test, the make-up ethylene charge consisting essentially of 100% ethylene was employed at a flow rate of 594.74 g per hour. The make-up oxygen gas charge comprising essentially 99.5% oxygen was employed at a flow rate of 848.88 g per hour. The third and final charge stream consisted essentially of 100% ethane gas at a flow rate of 9.08 g per hour. A recycle gas at a flow rate of 22,836.2 g per hour was mixed with the make-up streams. The molar composition of the recycle gas comprised 15.2% ethylene, 8.0% oxygen, 7.5% carbon dioxide, 17% argon, and 52.3% ethane. The resulting total feed, at a flow rate of 24,289 g per hour, was introduced into the reactor, which contained the same type catalyst and was maintained at the same temperature and pressure conditions as in the reference run. The molar composition of the total feed was 17% ethylene, 11% oxygen, 7% carbon dioxide, 16% argon and 49% ethane. Ethylene dichloride inhibitor, in an amount of 15 ppm by weight, was added to the reaction gas. The Δ EO value determined for this test was 1.92, while the overall yield was 68.6%.

A second test according to the invention was also conducted with ethane present in the total feed, in substantial amount as ballast, but with an increased ethylene concentration. The make-up ethylene charge in this test consisted essentially of 100% ethylene at a flow rate of 658.3 g per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen and had a flow rate of 944.32 g per hour. An independent make-up charge of essentially 100% ethane was also employed at a flow rate of 9.08 g per hour.

A recycle gas, at a flow rate of 22,677.3 g per hour, was mixed with the make-up charge streams. This recycle gas had a molar composition of 23.6% ethylene, 7.7% oxygen, 7.6% carbon dioxide, 14% argon, and 47.1% ethane. The total feed to the reactor, at a flow rate of 24,289 g per hour, had a molar composition of 25% ethylene, 11% oxygen, 7% carbon dioxide, 13% argon, and 44% ethane. Ethylene dichloride in an amount of 15 ppm by weight was introduced into the reactor as an inhibitor. The Δ EO value for this test was determined to be 2.13, while the overall yield was 68.6%.

The composition and results of the reference tests and of the tests conducted in accordance with the invention are provided below in Table I, for ease of comparison:

TABLE I

	Prior art Reference test	According to invention	
		Test No. 1	Test No. 2
Ethylene	17	17	25
Oxygen	7.5	11	11
Carbon dioxide	7	7	7
Argon	30	16	13
Nitrogen	38.5	--	--
Ethane	--	49	44
Ethylene dichloride	0.5 ppm	15 ppm	15 ppm
Δ EO	1.75	1.92	2.13
Overall yield	68.6%	68.6%	68.6%

Note. The components of the reaction gas mixture are given in terms of mol or volume %, except ethylene dichloride, which is expressed in terms of parts per million by weight.

A review of the results in Table I conclusively shows that the utilization of ethane as a major component of the total feed provides a significant improvement in productivity of ethylene oxide, of the order of 10%, without any sacrifice in overall yield. This improvement appears to be directly attributable to the increased oxygen concentration in the reaction gas mixture. It should be noted that, according to test No. 2, where the reaction conditions are substantially the same, with the only exception of increased ethylene concentration in the reaction gas mixture, even further improvement in ethylene oxide productivity is obtained, with the productivity improvement in test No. 2 being of the order of 22%.

Although the invention has been described relative to some specific examples, it will be readily apparent to those skilled in the art that various modifications in composition and procedure may be made to suit specific requirements without deviating from the spirit or scope of the invention as defined in the attached claims.

CLAIMS

1. Process for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, characterized by the fact that ethane is used in an amount of at least 10 mol% in the oxidation reaction mixture.

2. Process according to claim 1, characterized by the fact that a substantial portion of the ethane is provided in the ethylene feed, with the ethane being present therein as an impurity.

3. Process according to claim 1, characterized by the fact that the ethane is provided by an independent ethane feed.

4. Process for the production of ethylene oxide by the silver catalyzed controlled oxidation of ethylene with molecular oxygen, characterized by the fact that a gas mixture is passed over a silver-containing catalyst in a reaction zone, under ethylene oxide forming conditions, with said gas mixture consisting of ethylene, oxygen, and at least 10 mol% of ethane.

5. Process according to claim 4, characterized by the fact that the feedstock comprises impure ethylene, which ethylene contains ethane as the major impurity.

6. Process according to claim 4, characterized by the fact that the feedstock comprises essentially ethane-free ethylene, and that ethane is introduced into the reaction gas from a separate source.

7. Process according to claim 4, characterized by the fact that the feedstock comprises ethylene containing ethane, as well as ethane from a separate source.

8. Process according to claim 4, characterized by the fact that the mixture contains a catalyst activity inhibitor.

9. Process according to claim 8, characterized by the fact that the inhibitor is present in an amount effective for the purpose of counteracting any selectivity reduction attributable to the presence of ethane.

10. Process according to claim 4, characterized by the fact that the feedstock comprises high purity oxygen.

11. Process according to claim 10, characterized by the fact that the oxygen has a purity of at least 85 mol%.

12. Process according to claim 4, characterized by the fact that the mixture comprises:

Ethylene	4-40 mol%
Oxygen	6-15 mol%
Ethane	10-80 mol%
Inhibitor	1-100 ppm by weight

13. Process according to claim 4, characterized by the fact that the mixture comprises:

Ethylene	6-35 mol%
----------	-----------

Oxygen	8-14 mol%
Ethane	20-70 mol%
Inhibitor	5-70 ppm by weight

14. Process according to claim 4, characterized by the fact that the mixture comprises:

Ethylene	15-30 mol%
Oxygen	10-13 mol%
Ethane	40-60 mol%
Inhibitor	10-20 ppm by weight

15. Process according to claim 4, characterized by the fact that the mixture comprises:

Ethylene	approximately 17 mol%
Oxygen	approximately 11 mol%
Ethane	approximately 49 mol%
Ethylene Dichloride	approximately 15 ppm by weight

16. Process according to claim 4, characterized by the fact that the mixture comprises:

Ethylene	approximately 25 mol%
Oxygen	approximately 11 mol%
Ethane	approximately 44 mol%
Ethylene Chloride	approximately 15 ppm by weight

17. Process according to claim 4, characterized by the fact that the mixture comprises feedstock and recycle gas.

18. Process according to claim 4, characterized by the fact that the reaction zone is maintained at a temperature in the range of about 150 to about 450°C, and at a pressure ranging from atmospheric to about 35 atm. abs.

19. Process according to claim 4, characterized by the fact that the reaction zone is maintained at a temperature in the range of about 200 to about 300°C, and at a pressure ranging from about 17.5 to about 24.5 atm. abs.

20. Any process, product, device, or combination thereof that is substantially as described hereunder.

Brussels, December 5, 1967

By: Company named: HALCON INTERNATIONAL, INC.

/Signature/